

Deviations from the mean field predictions for the phase behaviour of random copolymers melts

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Abstract. – We investigate the phase behaviour of random copolymers melts via large scale Monte Carlo simulations. We observe macrophase separation into A and B-rich phases as predicted by mean field theory only for systems with a very large correlation λ of blocks along the polymer chains, far away from the Lifshitz point. For smaller values of λ , we find that a locally segregated, disordered microemulsion-like structure gradually forms as the temperature decreases. As we increase the number of blocks in the polymers, the region of macrophase separation further shrinks. The results of our Monte Carlo simulation are in agreement with a Ginzburg criterium, which suggests that mean field theory becomes *worse* as the number of blocks in polymers increases.

Introduction. – In polymeric systems one often encounters phase equilibria in mixtures with a large number of components. For instance, polydispersity (i.e. a continuous distribution of chain lengths) alters the phase equilibrium between a dense polymer phase and its vapour. Random AB copolymers constitute another example of such mixtures, each sequence of A's and B's represents a different component. The phase behaviour of random copolymers has attracted abiding interest, because these systems are produced commercially in large amounts and exhibit a rich phase behaviour. Mean field calculations [1, 2] predict a disordered phase, a macrophase separated phase and a disordered microphase separated phase, as a function of the incompatibility χ of the constituents A and B and the correlation λ along the polymers.

We present the first Monte Carlo study of the phase behaviour of random copolymers melts and compare our results to the mean field predictions. For rather short chain lengths we observe all three phases predicted by the mean field theory, but the region of stability of the macrophase separation is much smaller than predicted. Increasing the chain length, we reduce the region of macrophase separation and increase the deviation from the mean field prediction. Our simulation results indicate that random copolymer melts are one of the very few dense polymer systems for which mean field predictions do not become accurate, even if the chains strongly interdigitate and interact with many neighbours. This finding is corroborated by the Ginzburg criterium [3].

The layout of our paper is as follows: In the next section we briefly describe the model and summarise the mean field results pertinent to our computer simulation study. We give some details about the simulation technique [4, 5] in the following section. The dependence of the phase diagram on the chain length and correlation length along the chain are discussed and our findings are rationalised in terms of a Ginzburg criterium. The manuscript closes with a discussion and an outlook.

Model and Mean Field Predictions. – We consider a dense mixture of linear random copolymers. All chains consist of a random sequence of Q blocks, each of which comprises either M monomers of type A or M monomers of type B. The sequence of Q blocks is characterised by the average composition f (fraction of A–monomers) and the correlation parameter λ . The sequences of the polymers are once built by a random polymerisation process and are then kept fixed. The probability P_{AB} for an A–block to be followed by a B–block is $P_{AB} = (1 - f)(1 - \lambda)$ and similarly $P_{BA} = f(1 - \lambda)$ (of course, $P_{AA} = 1 - P_{AB}$ and $P_{BB} = 1 - P_{BA}$). For $\lambda = 1$, blocks are completely correlated and the model describes a binary mixture of homopolymers. For $\lambda = -1$ the polymers consist of a strictly alternating sequence of A and B–blocks. In the following, we only consider the symmetric case $f = 1/2$ and we denote the polymer length by $N = QM$.

A and B–monomers repel each other, and the strength of the repulsion is parameterised by the Flory–Huggins parameter χ . Upon increasing χ , monomers of the same type segregate to lower the energy, and a rich phase behaviour is anticipated: Within the mean field approximation, Fredrickson, Milner, and Leibler [2] have calculated the free energy as a functional of the local composition $m(\mathbf{r}) = \phi_A(\mathbf{r}) - f$. For symmetric composition $f = 1/2$ it takes the form:

$$\frac{\mathcal{F}[m]}{k_B T \rho} = \frac{1}{V} \int d\mathbf{r} \left\{ (\chi_c - \chi) m^2 + \frac{4Q}{M\Lambda^2} m^4 + \chi_c \Gamma R_M^2 (\nabla m)^2 \right\}, \quad (1)$$

with $\Lambda = (1 + \lambda)/(1 - \lambda)$ and $\Gamma = (\lambda - \lambda_L)(\lambda + 2 + \sqrt{3})/[3(1 - \lambda^2)]$ for $\lambda^Q \ll 1$ [6]. R_M is the radius of gyration of a block. We assume $\lambda > \lambda_L = -2 + \sqrt{3} \approx -0.268$. Otherwise the coefficient of the square gradient term becomes negative and higher derivatives have to be considered.

At large incompatibility $\chi > \chi_c = 2/(M\Lambda)$, there is macrophase separation. Since the typical excess of A–monomers along a random copolymer is of order M/\sqrt{Q} the difference of the composition of the two phases also is only proportional to $1/\sqrt{Q}$ and phase separation reduces the energy of a single molecule by χM independently of the number Q of blocks per chain.

If χ is increased further, mean field theory predicts a second transition at χ_m where the two coexisting phases remix and form a microphase with no long ranged order. The characteristic length scale is set by the size R_M of a block and becomes smaller as we increase χ . The stability region of the macrophase separation decreases with the number of blocks; $\Delta t \equiv [\chi_m - \chi_c]/\chi_c$ is of the order $1/Q$.

It has been suggested that the role of fluctuations on the macrophase transition is similar to that of a binary mixture of homopolymers [2, 7]. In the homopolymer blend, there is only a very narrow non–classical region about the critical line that is inversely proportional to the chain length. For smaller correlations, stronger fluctuation effects are anticipated. In particular, the isotropic Lifshitz point at $\lambda = \lambda_L$ does not survive fluctuations [8] and fluctuations will change the order of the transition towards the microphase separated state from second to first [9–12].

Simulation Technique. – In the Monte Carlo simulations we employ the bond fluctuation model [13]. Monomers are represented by a cube on a 3D lattice and block its 8 corners from further occupancy. Monomers along a polymer are connected via bond vectors of length 2, $\sqrt{3}$, $\sqrt{5}$, 3 and $\sqrt{10}$. Interactions between monomers are modelled by a square well potential, which extends over the nearest 54 lattice sites. Monomers of different types repel each other with an energy ε_0 [14] and we define $\varepsilon = \varepsilon_0/k_B T$. This is related to χ through $\chi \simeq z\varepsilon$ where z is the number of intermolecular contacts. This model is an ideal testing bed for comparing simulations to the predictions above. The phase behaviour [15] and interface properties [16] of homopolymer mixtures and diblock copolymers [17] have been studied in the framework of this coarse grained model, and the simulation results have been compared to mean field predictions of the Gaussian chain model without any adjustable parameter.

In fact, Swift and Olvera de La Cruz [18] have used this model to investigate the behaviour of random copolymers. Using a local hopping algorithm, they found evidence for microphase separation at $\lambda = 0$ and a substantially decrease of the centre of mass diffusion at low temperatures. The slow relaxation corroborates a frozen-in, glassy structure predicted for low temperatures [19–21]. Extracting the phase behaviour and its dependence on the chain length poses a challenge for computer simulations: (i) One needs an efficient update of the chain conformations on the lattice to reduce the protracted long time scales associated with the (almost) frozen structure. (ii) The canonical ensemble is not well suited to investigate macrophase separation, because the two coexisting phases (and the interfaces separating them) are simultaneously present in the simulation cell. Accurately extracting the phase boundaries from simulations in the canonical ensemble would require inaccessibly large simulation cells since we expect weak segregation and wide interfaces. (iii) Due to the finite size of the system, the actual mixture produced by the random polymerisation process deviates from the mean composition defined by f and λ . One should *a priori* average over different realisations of the disorder, considerably increasing the CPU time required. Due to these computational difficulties, the way how fluctuations modify the phase behaviour predicted by mean field calculations could not be addressed in computer simulations.

To cope with the freezing of the structure, we employ a recently devised “wormhole” algorithm [4], which generalises and improves the slithering snake algorithm for random copolymers. Additionally, we use parallel tempering [22] to help the structure equilibrate at low temperatures (large χ). Generally, a grand-canonical simulation of a random copolymer mixture is not straightforward, because the mixture contains a large number of components (i.e. different sequences). The density of the species is set by the disorder, but their (temperature dependent) chemical potentials are unknown. If we restrict ourselves, however, to symmetrical composition $f = 1/2$, the system is invariant under exchanging $A \rightleftharpoons B$ monomers. Hence, it is possible to switch the identity of all monomers along one chain (and accept this Monte Carlo move according the Metropolis criterium). This moves relaxes the composition of the system, which is the order parameter of the macrophase separation. Owing to this symmetry, the system is either symmetric (disordered or microphase separated state) or it coexists with its symmetric in the two phase region. Standard finite size scaling techniques of grand-canonical simulations can be applied to accurately locate the phase boundaries. Finally to avoid the average over a large number of realisations of the disorder (i.e. the sequences of the polymers), we devised a method to produce a “generic” random copolymer mixture which does not present random fluctuations. More details on the simulation technique will be published elsewhere [5].

Results. – We have simulated different sets of the parameters Q and M , for a large number of values of ε and λ . We found the following: at small ε (i.e. high temperature) the

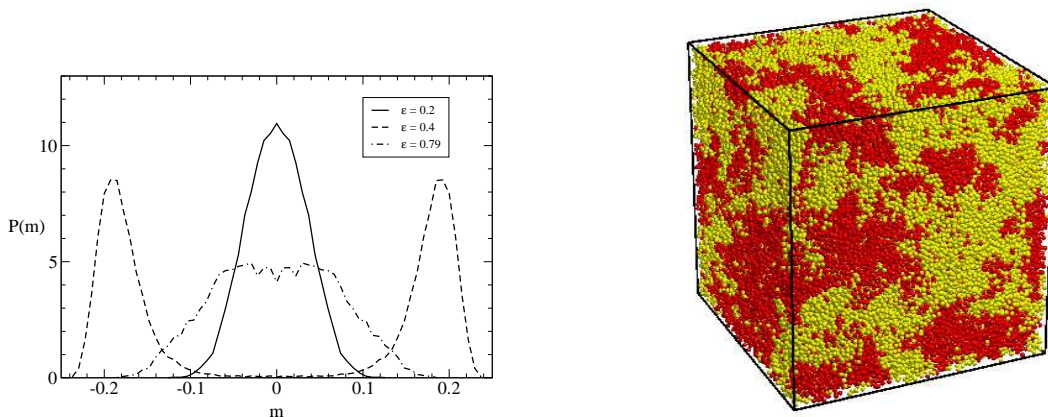


Fig. 1 – *Left*: Distributions of m (the composition of the system), for different values of the incompatibility ε . The data here corresponds to $M = 1$, $Q = 20$, $\lambda = 0.85$ in simulation box of size 80^3 . *Right*: A snapshot of the same system for $\varepsilon = 0.79$ (in a 120^3 box). The monomers are represented by small spheres and the bonds are not shown. The colors correspond to the nature of the monomers (A or B). The typical end-to-end distance for one polymer is here roughly one 13th of the box size.

system is homogeneous. Provided that λ is large enough, the system phase separates when one increases the incompatibility (i.e. decrease the temperature). Finally, at an even larger ε , the system remixes. This is determined by looking at the distribution $P(m)$ of the composition (Fig. 1). The macrophase separation is a standard Ising-like second order phase transition and we accurately determine the transition temperature by mapping $P(m)$ onto the known distribution of the 3d Ising universality class. From a numerical point of view, the nature of the remixing transition is unclear, it could be a simple second order phase transition with strong finite size effects or there could be a region where more than two phases coexist. Hence, error bars in the temperature of remixing are much larger than for the unmixing at higher temperature. The snapshot in Fig. 1 shows a typical configuration in the low temperature phase. Large domains can be observed which have a typical length scale several times larger than the end-to-end distance of one polymer. On the other hand, if λ is small, we do not see any phase transition. The distribution $P(m)$ simply broadens and narrows again as the temperature decreases.

We determined the phase boundaries for different values of M and Q . The topology of the phase diagram we found is similar to the one of a ternary mixture of two homopolymers and a diblock copolymer (it is actually the special case $Q = 2$ and large M). The results are shown in Fig. 2 using the scaling of mean field theory. On the left part of Fig. 2 (varying Q at constant M), we see that the phase boundaries do not seem to scale as expected by mean field. The scaling in ε does not apply and as one increases Q the minimal value of λ for which we observe a phase separation goes to larger values of λ instead of going to λ_0 .

In view of the unexpectedly large deviations between our simulations and the mean field predictions, we assess the validity of the latter approach via the Ginzburg criterium. The mean field approximation is accurate, if fluctuations $\langle m^2 \rangle$ of the composition in a volume of the size of the correlation length ξ are small compared to the difference of composition between the two coexisting phases. Using the mean field functional (equation 1) we calculate the composition of the two coexisting phases: $m = \pm \sqrt{\Lambda|t|/4Q}$ where $t = (\chi_c - \chi)/\chi_c$ denote the distance to the onset of macrophase separation. The correlation length above the critical temperature is

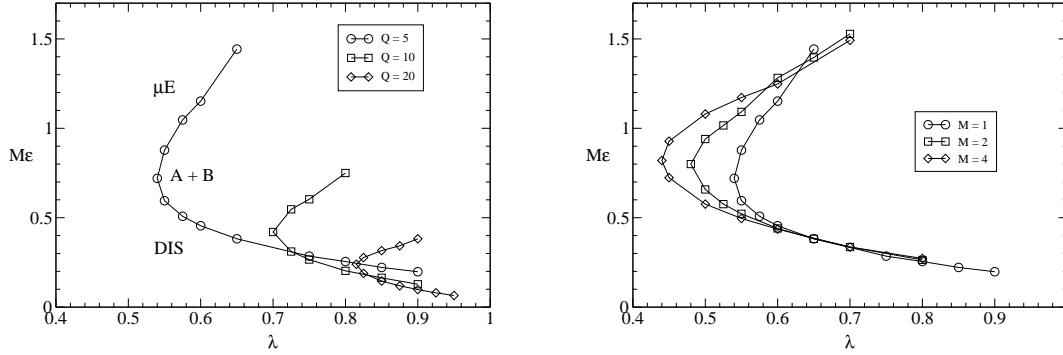


Fig. 2 – *Left*: Phase boundaries as a function of the correlation parameter λ and the incompatibility ϵ for different values of Q at constant $M = 1$. The disordered phase (DIS), the macrophase separated phase (A+B) and the microemulsion-like phase (μE) are respectively below, on the right and above the curves. *Right*: The same for different values of M at constant $Q = 5$.

given by $\xi^+ = R_M \sqrt{\Gamma/|t|}/2$ and the critical amplitude is reduced by a factor $\sqrt{2}$ below the critical point. The scale of the correlation length is set by the size of an individual block R_M and does not depend on the number Q of blocks. The susceptibility above the critical point takes the form $V\langle m^2 \rangle^+ = M\Lambda/[4\rho|t|]$ and the critical amplitude is a factor 2 lower in the macrophase separated state. Using these expressions, we obtain for the Ginzburg criterium:

$$t \gg Gi = \frac{16}{\Gamma^3} Q^2 \left(\frac{M}{\rho R_M^3} \right)^2 \sim Q^2 \frac{1}{M}. \quad (2)$$

The last factor measures the inverse degree of interdigitation of blocks. This factor resembles the behaviour of binary homopolymer blends, except for the important difference that it is only proportional to the inverse length of a block ($1/M$) and not to that of the whole chain ($1/MQ$). In marked contrast to the homopolymer blend, the Ginzburg number increases and the region of validity of the mean field theory decreases as we increase the number Q of blocks. Our finding disagrees with previous estimates which assumed a behaviour similar to a binary mixture of homopolymers.

We expect fluctuations to shift the macrophase separation to larger values of the incompatibility by an amount $\delta t \sim QM/\rho R_M^3$. For long random copolymers (i.e. large Q) this shift exceeds by far the stability range of the macrophase separated state which is, in the framework of the mean field calculation, of order $\Delta t \sim 1/Q \ll \delta t$. Of course, fluctuations also affect the onset of microphase separation and shift it to higher values of ϵ . Our simulations, however, indicate that the stability region of the macrophase separation decreases with increasing number of blocks Q .

On the other hand, the large M behaviour (at constant Q) approaches the mean field predictions as can be seen on the right part of Fig. 2. This is consistent with the fact that $G_i \rightarrow 0$ as $M \rightarrow \infty$ which indicates that mean field should be correct in this limit. This limit is not generic for copolymers built by random polymerisation of blocks because the size M of the blocks would have to increase with increasing number of blocks. Nevertheless the case $Q = 2$ corresponds to a ternary mixture of two homopolymers and a diblock copolymer in which case the $M \rightarrow \infty$ is the relevant limit and is known to approach mean field [23].

Summary. – Using extensive Monte Carlo simulations, we have studied the phase diagram of random copolymer melts. The region where macrophase separation occurs is much

smaller than predicted by mean field, and this region further shrinks as the number Q of blocks in the polymers increases. We can then conclude for this system that surprisingly, mean field becomes worse as the size of the polymers increases. On the other hand, the mean field behaviour is recovered in the limit of large blocks ($M \rightarrow \infty$). Both observations are corroborated by the Ginzburg criterium.

The unexpected observation, that mean field theory fails to describe the qualitative behaviour in the limit of infinitely long chains, is traced back to the weak segregation and the small correlation length due to the disorder in the polymer sequences.

Future work should address three subjects not treated here: (i) The nature of the low temperature phase, in particular its spacial structure. (ii) The type of the transition between the macrophase separated region and the low temperature phase. We are currently investigating the possible existence of a 3 phase region, using grand canonical simulations with chemical potentials (at small Q to reduce the number of different chemical species). (iii) The scaling of ε in the large Q regime.

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